

Electronic Supplementary Information

Green Approach: Scalable Dry Media Synthesis of γ -TaON Photocatalyst for Solar H₂ Production and Rhodamine B Degradation

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Experimental:

An aqueous suspension of Rhodamine B (100 ml, 10 ppm) was used as a model organic dye pollutant for photocatalytic degradation under natural solar light. The photocatalytic activity was carried out in quartz reactor having a flat optical window with water circulation system from outside the reactor to maintain constant reaction temperature. Before irradiation with solar light, the suspension was stirred in the dark for 45 min to ensure the establishment of an adsorption/desorption equilibrium. Prior to irradiation, one aliquot was collected and named as a zero reading i.e. 0 min and it is analyzed by UV-Vis spectroscopy. Then, the suspension was irradiated with solar light for stipulated time. During irradiation process, the aliquots of reaction mixture were collected at regular intervals and allow to settle the suspended photocatalyst. Prior to UV-Visible analysis, the photocatalyst was separated from aliquots by centrifugation. The clear solution (supernatant) was analyzed using UV-Visible spectrophotometer. The change in spectral intensity of RhB (decrease in concentration) with irradiation time (min) was monitored under identical experimental condition. Percent degradation (%) with time (min) was calculated and compared with blank.

Photocatalytic H₂ production via H₂O splitting

Along with dye degradation, synthesized catalyst was also tested for photocatalytic H₂ production via H₂O splitting using triethanolamine (TEOA) as a sacrificial agent. For comparative study, photocatalytic activity is tested using 300 W Xenon lamp

and natural solar light. Xenon lamp (Newport Corporation) was used with UV Schott GG 400 filter with cut-off wavelength of 400 (± 6 nm) to get rid of all UV radiations. All the experiments were performed in air tight cylindrical quartz reactor with cooling water jacket outside the reactor to maintain constant reaction temperature. The reactor was having provision of gas sampling during photo-reaction. The reactions under natural solar light were carried out at ambient conditions in sunny days (March to May months) between 10 am to 3 pm at Pune, located in Maharashtra, state of India. Average intensity of solar light reaching to the surface of earth was 1,74,000 Lux measured using digital Lux meter.

In a typical photocatalytic experiment, specific amount (15 mg) of photocatalyst was dispersed in 25 ml 20% (v/v) triethanolamine aqueous solution. Before illumination, the suspension was sonicated for 5 min in order to make better dispersion of photocatalyst into reaction mixture. Then, photo-reactor was thoroughly degassed with UHP N₂ gas (99.999%) with stirring for removal of dissolved gases as well as gases from headspace of the reactor. Finally, the solution was exposed to solar light and xenon lamp with constant stirring for 4 hrs. At regular intervals, evolved gases collected in the reactor were analyzed using gas chromatography (GC). Prior to analysis, the GC instrument was calibrated using standard sample of H₂ gas. Total H₂ gas produced in headspace of the reactor was calculated from the area under the curve of H₂.

Result and discussion:

ESI Fig.1 shows XRD of TaCl₅ and guanidine carbonate (1:14) heated at 650 °C for different time such as 1, 2, 3 and 4 hrs. This indicates that decrease in diffraction peaks after 2 hrs and therefore, we have used 650 °C for 2 hrs as an optimum time for all future calcination reactions.

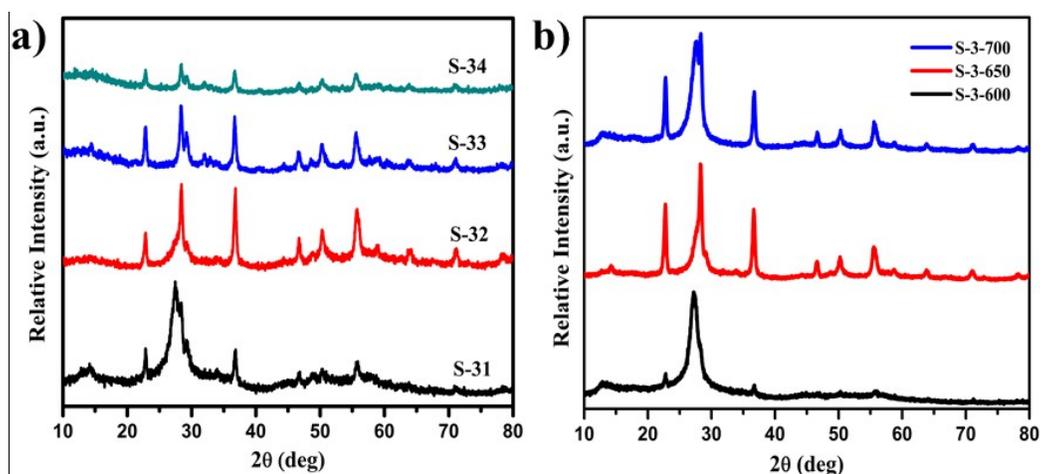


Figure 1: XRD pattern of TaCl₅:guanidine carbonate (1:14) heated a) at 650°C for different time such as 1, 2, 3 and 4 hrs named as S-31, S-32, S-33 and S-34, respectively b) at different temperature such as 600, 650 and 700 °C named as S-3-600, S-3-650 and S-3-700, respectively.

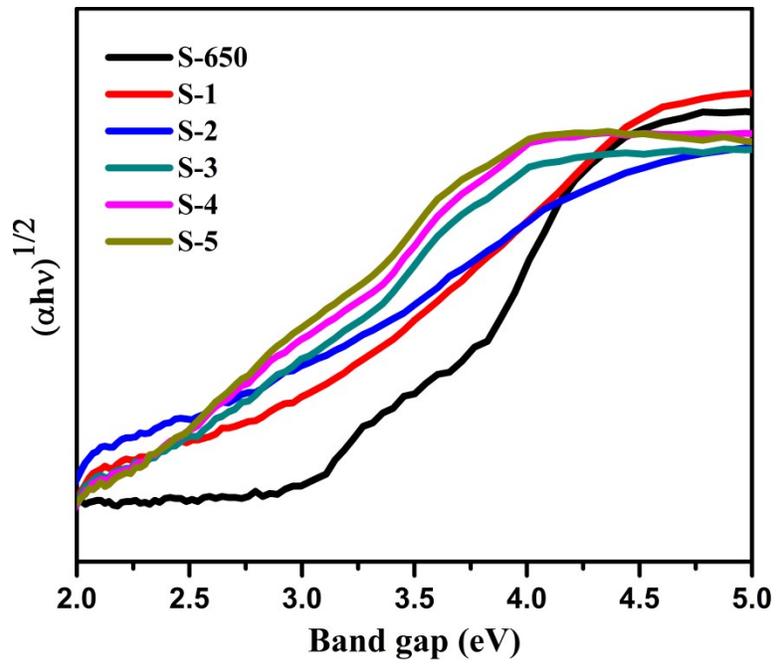


Figure 2: Tauc plot of pure Ta₂O₅ and TaON samples.

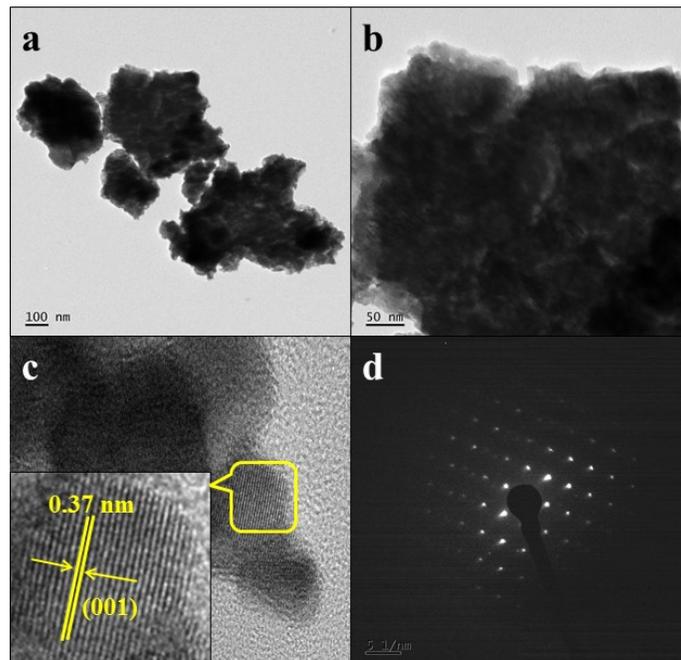


Figure 3: FETEM images of Ta₂O₅ (S-650) sample.

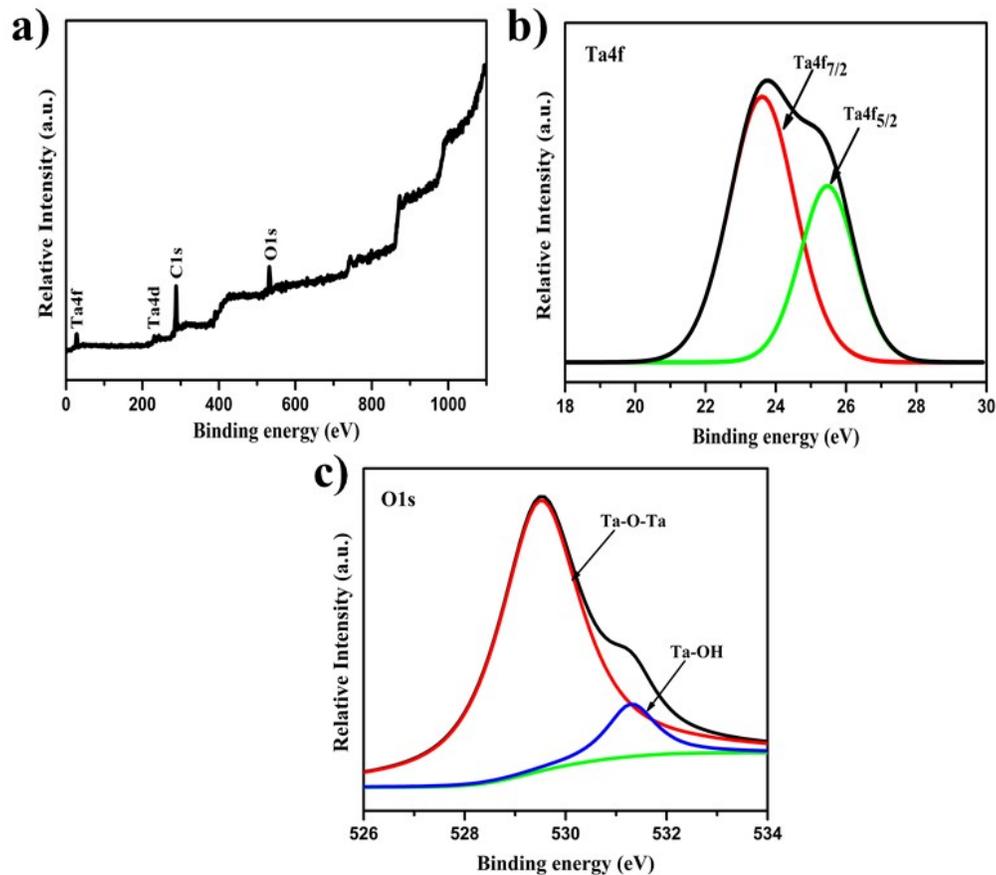


Figure 4: XPS of Ta₂O₅ (S-650) sample.

Guanidine carbonates plausible decomposition mechanism reactions:

Guanidine carbonate ($C_3H_{12}N_6O_3$ / $(C(NH_2)_3)_2CO_3$) having potential as solid ammonia (NH_3) source which releases high amount of NH_3 starts at relatively lower temperature.¹ At 185 °C, melamine forms by releasing NH_3 and CO_2 which contains alternating C and N atom bonds, is characterized by high thermodynamic stability. Subsequent heating to higher temperature, melamine undergoes progressive endothermic condensation with the release of NH_3 and forms melam, melem and melon products.² Melamine condensation start above 300 °C to form melam (melamine dimer $(C_3N_3)_2(NH)-(NH_2)_4$) which is metastable intermediate. Melam readily undergoes transition to melem $C_6N_7(NH_2)_3$; thermodynamically stable heptazine-based compound formed at about 390 °C.³ Further heating of melem leads to oligomers (dimers, trimers, tetramers, etc. which are created in the temperature range of 400–500 °C) and eventually polymeric heptazine-based compounds called as melon, poly(aminoimino)heptazine, $[C_6N_7(NH_2)NH]_n$, which is a linear and/or cyclic structure.⁴ It is the condensation product of heptazine moieties (bridged by NH groups). Polymeric graphitic carbon nitride (g- C_3N_4) can be interpreted as a final de-ammoniation polycondensate product of melamine forms at around 520-540 °C becoming unstable slightly above 600 °C. It is important to note that the high-temperature de-ammoniation (above 600 °C) results in the residue-free decomposition, mainly into volatile CNH, NH_3 and C_2N_2 species.⁵ Kimura et al. showed crystallization temperature of Ta₂O₅ film grown by reactive sputtering lies between 650-700 °C.⁶

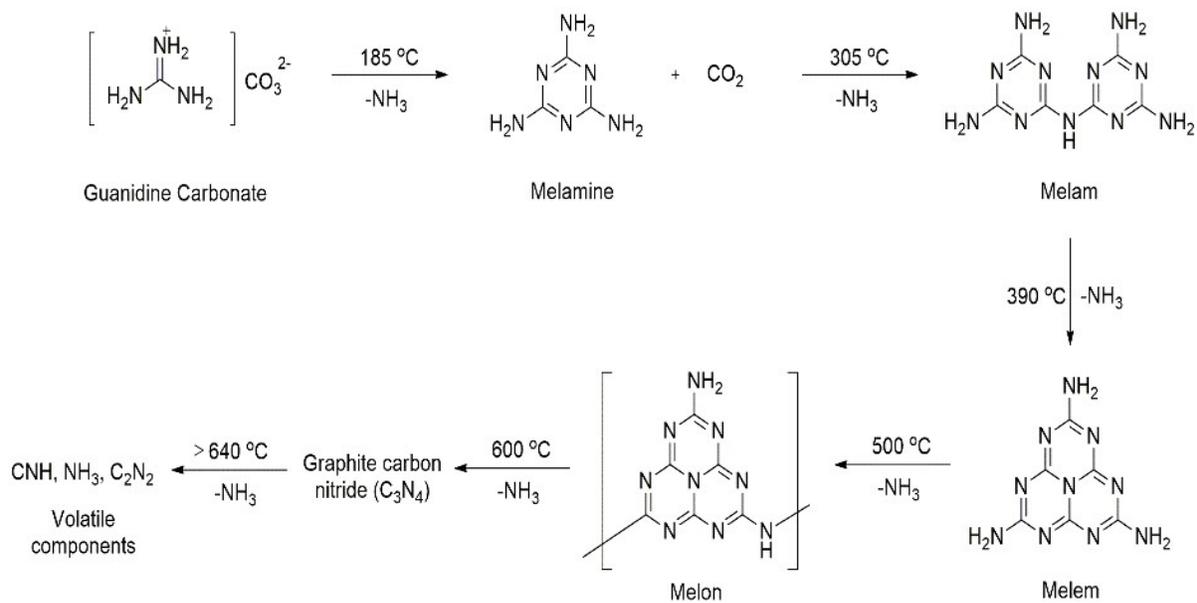


Figure 5: Schematic mechanism of decomposition of guanidine carbonate.

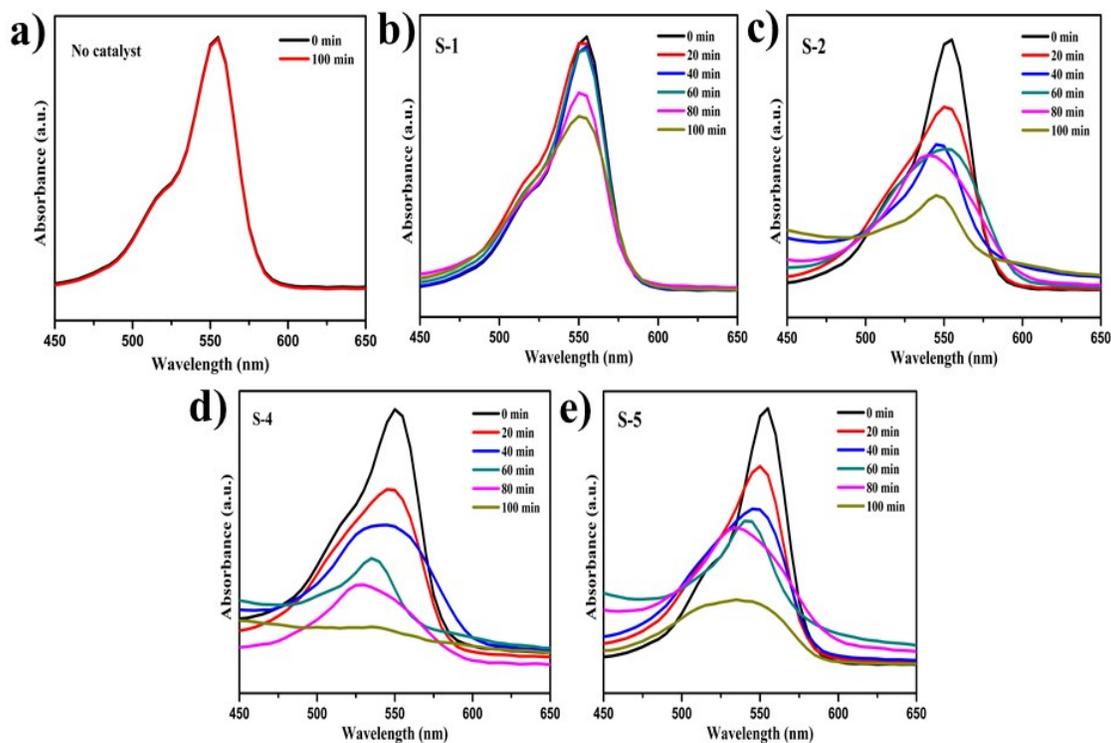


Figure 6: UV-Visible spectra of photo-degradation of RhB solution (10 ppm) under natural solar light irradiation over different photocatalysts.

Table 1: Different photocatalyst with their band gaps and rate of H₂ production under natural solar light and xenon lamp

Sr. no.	Photocatalyst	Band gap (eV)	H ₂ under xenon lamp (μmol/0.1g/hr)	H ₂ under solar light (μmol/0.1g/hr)	RhB degradation (%)
1.	S-650	3.75	2.7	3.58	7.09
2.	S-1	2.85	445.5	658.4	31.4
3.	S-2	2.81	468.1	868.5	62.5
4.	S-3	2.73	833.6	1393.6	99.8
5.	S-4	2.69	705.4	970.2	86.3
6.	S-5	2.65	624.1	866.7	9.6

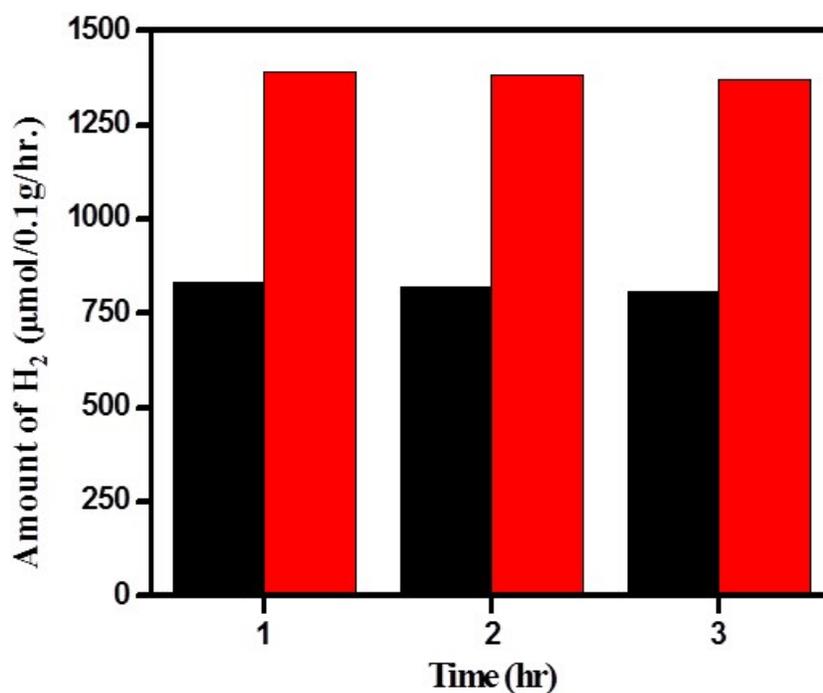


Figure 7: Cyclic stability study of H₂ generation over S-3 photocatalyst

under natural solar light and xenon lamp.

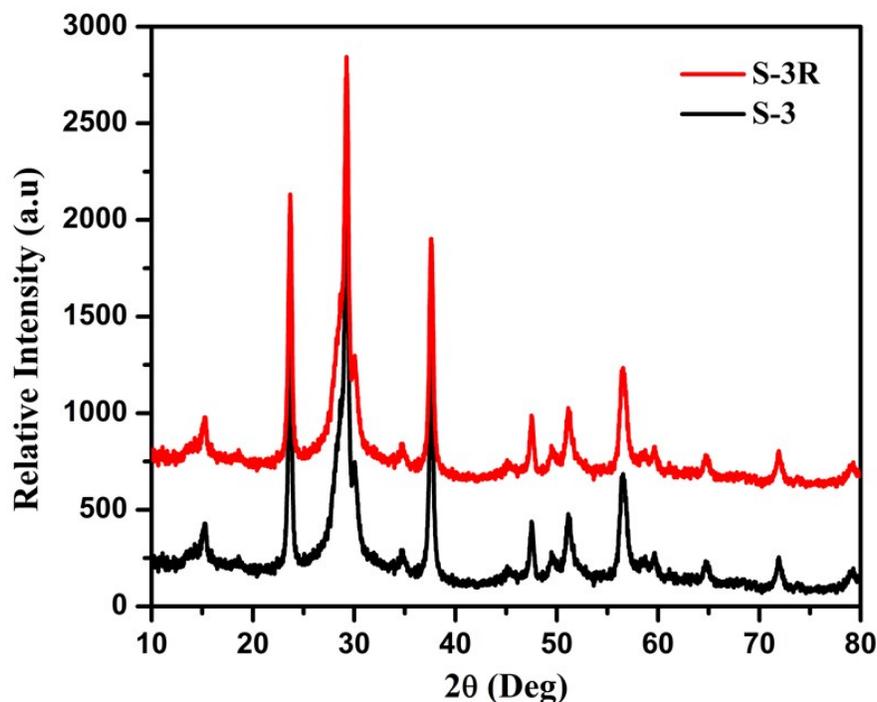


Figure 8: XRD of as-prepared S-3 and sample after 3 cycles of photocatalytic reactions.

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